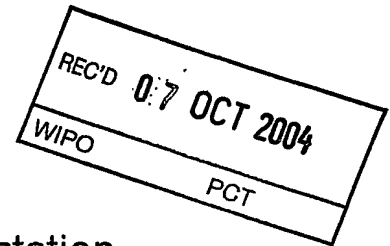




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Flame retardant compositions

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## FLAME RETARDANT COMPOSITIONS

The present invention is directed to a method of flame retarding a polymeric substrate using a specific group of compounds as flame retardants, to flame retardant  
5 compositions as well as to novel compounds usable as flame retarding compounds.

### Background of the Invention

Typically, inorganic and organic flame retardant (FR) compounds have been used for flame retarding various type of polymers. The main types of FR's include halogenated hydrocarbons, phosphorous containing compounds, metallic compounds  
10 such as metal oxides and hydroxides, and melamine derivatives. Halogenated FR's are very commonly used due to their effectiveness. Nevertheless, the use of halogenated compounds has generally become of an environmental concern.

To diminish the problems relating to halogenated FR's synergists are often used in combination with halogenated FR's. Synergists are compounds which enhance the  
15 flame retarding properties of the halogenated FR's and thus enable to use the halogenated FR's in substantially reduced amounts. Synergistic compounds encompass a group of compounds known as "free radical initiators" which include organic peroxide (see e.g. US 3058926), dibenzyl (see e.g. US 3271333 and US 3420786), disulfide (see e.g. US 3284544), hydrazone (see e.g. US 3269962), and azo com-  
20 pounds (see e.g. US 4237179, US 3897373, US 4486347 and FR 1425563). See also US 347204, US 3296340, GB 1015217, US 4337319, WO 03046016, US 4710528, EP 1239005. Accordingly, the synergists are used only in combination with other FR's, and typically with said halogenated FR's, and/or they may be halogenated by themselves. The azo compounds have been used e.g. as an azo dye with  
25 an additional function as a FR synergist, and typically complexed with a metal, e.g. Cu or Cr.

Many of these free radical initiators have also been used for other purposes, i.a. for controlling certain properties of a polymer during a polymerisation process or for grafting a polymer, as foaming agent or as dyes as mentioned above etc. (see US  
30 5079283, WO 00/19452, US 3826764 and also EP 402 904 and EP 0073488).

Non-halogenated N-hydrocarbyloxy hindered amines (NOR-hindered amines) have also been proposed for solving the problem. These can be used alone, e.g. in place of halogenated FR's, or as a synergist for FR applications (see e.g. WO 99/00450).

5 There still exists a high demand for effective non-halogenated flame retarding compounds, which would provide an industrially and environmentally desirable alternative for the halogenated FR compounds.

### **Object of the Invention**

The object of the present invention is to provide further non-halogenated compounds which are free from heavy metals and can be used as effective flame retardants as such, e.g. in place of the conventional FR compounds, such as halogenated FR's.

### **Detailed Description of the invention**

15 The inventors have unexpectedly found that a specific group of non-halogenated azo, hydrazine and peroxide derivatives show themselves flame retarding efficacy when used e.g. in polymeric applications, i.e. they need not to be combined e.g. with other FR's, such as conventional organic or inorganic halogenated FR compounds or with phosphorous, antimony or metal hydroxide FR compounds. Advantageously, they can be used in place of the halogenated, e.g. the conventional brominated or chlorinated FR's.

20 The present finding is surprising, since in the prior art "free radical initiators", i.e. dibenzyl, peroxide, azo etc. compounds known in the field are disclosed to be useful only in combination with other, particularly with halogenated, FR's. According to the prior art they act by enhancing the properties of the halogenated FR's. Thus, the now found FR efficacy of the present compounds is a new property which is contrary to the prior art teaching or belief. More surprisingly, the compounds of the invention possess FR activity at industrially acceptable levels, although they are non-halogenated. Furthermore, the FR efficacy can be achieved in desirable low amounts of the present compounds, and, advantageously, if needed, even higher amounts can be used without impairing the properties of the polymer in the FR compositions of the invention.

30 The features of the invention are defined in claims.

Accordingly, the invention provides a group of compounds of formula (I'), which bear a specific -Z<sub>1</sub>-Z<sub>2</sub>-Z<sub>3</sub>- functionality and contain no halogen substituents with surprisingly good FR efficacy for flame retarding polymeric substrate. Said FR activity has not been disclosed in the prior art for the said compounds:

- 5 The present non-halogenated compounds have the formula (I'):



wherein Z<sub>1</sub> and Z<sub>2</sub> are both NR<sub>1</sub> and Z<sub>3</sub> is C or N; or Z<sub>1</sub> and Z<sub>2</sub> are both O and Z<sub>3</sub> is C; r is 0, when Z<sub>3</sub> is N, and r is 1, when Z<sub>3</sub> is C;

- 10 the two R<sub>1</sub>'s form together a bond or each R<sub>1</sub> is independently H or forms a bond together with R<sub>2</sub> present at the adjacent C-atom or, respectively, Z<sub>3</sub>;

each R<sub>2</sub> independently forms a bond or is a monovalent radical as defined for R<sub>3</sub> and R<sub>4</sub> below;

- 15 each R<sub>3</sub> and R<sub>4</sub> is independently a monovalent radical selected from H, optionally substituted alkyl, optionally substituted alkyl interrupted with one or more O, N and/or S atom(s), optionally substituted cycloalkyl, optionally substituted cycloalkylalkyl, optionally substituted aryl, optionally substituted arylalkyl, optionally substituted alkoxy(alkyl)<sub>n</sub>, optionally substituted aryloxy(alkyl)<sub>n</sub>, optionally substituted arylalkyloxy(alkyl)<sub>n</sub>, optionally substituted alkenyl, optionally substituted alkenyloxy(alkyl)<sub>n</sub>, optionally substituted alkynyl, optionally substituted alkynyloxy(alkyl)<sub>n</sub>, optionally substituted heterocyclyl(O)<sub>s</sub>(alkyl)<sub>n</sub> with one to four hetero atoms selected independently from N, O and S; R-Y-C(O)-(alkyl)<sub>n</sub> or R-C(O)-Y-(alkyl)<sub>n</sub>, wherein R is H, or alkyl, alkenyl, cycloalkyl, aryl or heterocyclyl as defined above, each of which is optionally substituted, Y is O or NH;

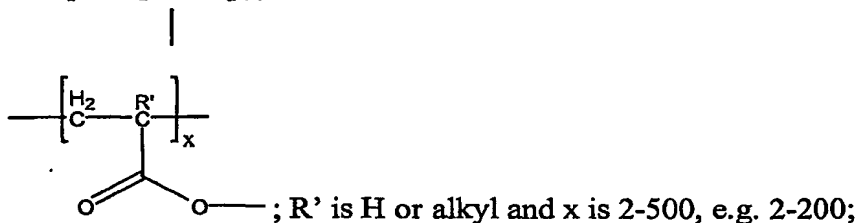
- 25 or at one or both of the C-atom and Z<sub>3</sub>, as given in the above formula (I'), R<sub>3</sub> and R<sub>4</sub> form together with said C-atom or, respectively, Z<sub>3</sub>, wherein they are attached to, an optionally substituted, saturated, partially saturated or aromatic, mono- or polycyclic ring system of 5 to 20 carbon and, optionally, hetero ring atoms, whereby the optional hetero ring atoms are selected from N, O and/or S; and R<sub>2</sub> is a monovalent radical as defined for R<sub>3</sub> and R<sub>4</sub> above, or forms a bond between the C-atom and Z<sub>1</sub> or, respectively, between Z<sub>3</sub> and Z<sub>2</sub>, or forms a bond in the ring system formed by R<sub>3</sub> and R<sub>4</sub> between said C-atom or, respectively, Z<sub>3</sub>, and a ring atom adjacent thereto;
- 30

each s and n is independently 0 or 1;

or  $Z_3$  forms together with  $R_2$ , if present,  $R_3$  and  $R_4$ , which are attached thereto, a group  $-R'_5([Z_1-Z_2-R_6-]_k Z_1-Z_2-R_5-H)_t$ , wherein each  $R'_5$  and  $R_5$  is independently optionally substituted alkyl, optionally substituted alkyl interrupted with one or more N, O and/or S, optionally substituted cycloalkyl, optionally substituted cycloalkylalkyl, optionally substituted cycloalkylalkylcycloalkyl, optionally substituted aryl, optionally substituted arylalkyl, optionally substituted arylalkylaryl, optionally substituted heterocyclyl, optionally substituted heterocyclylalkyl or optionally substituted heterocyclylalkylheterocyclyl, each  $R_6$  independently has a meaning as given for  $R'_5$  and  $R_5$  above,  $Z_1$  and  $Z_2$  are each independently as defined above,  $t$  is 1-3 and  $k$  is chosen so that the molecular weight of the resulting compound of formula (I') is within 200 to 10000 g/mol, e.g.  $k$  is 0-500;

or  $Z_3$  together with  $R_2$ , if present,  $R_3$  and  $R_4$ , which are attached thereto, represent a linking group  $-R_8-$  to form  $R_2R_3R_4C-Z_1-Z_2-R_8-[U]_x$  which denotes a recurring structural unit of a polymer, wherein  $R_8$  is a linking bond or alkyl, cycloalkyl, heterocyclyl or aryl;

$U$  is  $[-CH_2-CR'-]_x$ ; or



or the two  $R_3$ 's, as given in the above formula (I'), form together with the  $-(R_2R_4)C-Z_1-Z_2-Z_3((R_2)_rR_4)-$  moiety an optionally substituted, saturated, partially saturated or aromatic, mono- or polycyclic ring system of 5 to 20 carbon and, optionally, further hetero ring atoms, whereby the further hetero ring atoms are selected from one or two of N, O and/or S; and wherein  $Z_1$  to  $Z_3$ ,  $r$  and  $R_2$  to  $R_4$  are as defined above;

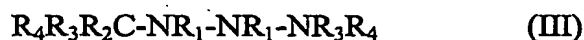
and the compound of formula (I') is selected from the following compounds of formulae (II)-(IV):

a compound of formula (II)



wherein the two  $R_1$ 's form together a bond, or each  $R_1$  independently is H or forms a bond together with  $R_2$  present at the adjacent C-atom as defined above;

a compound of formula (III)



wherein the two  $R_1$ 's form together a bond; or

a compound of formula (IV)



wherein in the above formulae (II)-(IV)  $R_1$  to  $R_4$  are defined as above;

as well as use of an oxide of N as  $Z_1-Z_3$ , a salt, an ester or an amide thereof, or of a mixture of two or more compounds of formula (I') as defined above.

- Generally, a group or a moiety of a group in the definitions of the substituents, i.a.  $R_2$  to  $R_6$ ,  $R'_5$ ,  $R_8$ ,  $R$ , said ring system formed by  $R_3$  and  $R_4$  and by the two  $R_3$ 's, is optionally substituted with one or more, e.g. 1-5, such as 1-3, substituent(s). Such "optional substituents" may be selected independently e.g. from alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkylalkyl, aryl, arylalkyl, alkoxy, aryloxy, heterocyclyl, -N(R)<sub>2</sub> wherein each R is independently as defined above, =O, -OH, -SH, COOH, R-  
 10 Y-C(O)-(alkyl)<sub>n</sub>, R-C(O)-Y-(alkyl)<sub>n</sub>, wherein R, Y and n are as defined above. Preferred "optional substituents" include -OH, -NH<sub>2</sub>, -COOH, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkylalkyl, aryl, arylalkyl, alkyl-C(O)-O-, alkenyl-C(O)-O-, such as acrylate, and/or alkyl-O-C(O)-. Any cycloalkyl, aryl or heterocyclyl as said "optional substituent" is also optionally substituted with an "optional substituent" as  
 15 defined above, e.g. with 1-3 OH, alkyl and/or alkenyl, such as CH<sub>2</sub>=CH-. In a further subgroup any optional substituents are as defined above except aryl or heteroaryl.

- The present invention covers all the possible stereoisomers of the compounds (I') including cis and trans isomers, and any mixtures of the isomers, such as trans isomers or mixtures of trans and cis isomers. The individual isomers may be obtained  
 25 e.g. by using corresponding isomeric forms as the starting material or by separating the desired isomer from a mixture of end products using conventional separation methods.

- 30 One preferable group of the compounds (I') are compounds of formula (I), wherein at least at one of the C-atom and  $Z_3$ , as depicted in the above formula (I'),  $R_3$  and  $R_4$

are independently other than H and  $R_2$  is H or a bond. Accordingly, the compounds (I) bear said specific substituent pattern at least at the C-atom or at  $Z_1$ , or at both. The compounds (I) have not been disclosed in the prior art as possessing any FR nor synergistic FR activity.

- 5 Below are listed further definitions for the substituents defined in formula (I'), which can be used alone or in any combinations for defining more specific preferable subgroups of formula (I') or (I), or of any other formula given below:

The invention covers acyclic compounds (I') or (I), for example those, wherein each  $R_3$  and  $R_4$  are independently a monovalent radical as defined above, or form together with  $Z_1$  a monovalent radical as defined above, or form together with C-atom and/or  $Z_1$ , wherein they are attached to, a ring system. The invention also covers cyclic compounds (I') or (I), i.e. the two  $R_3$ 's form together a ring system as defined above. The compound of formula (II) or (III) includes an acyclic or a cyclic azo compound, hydrazine, hydrazone, azine or triazene, or an oxide of an azo compound; and the compound of formula (IV) includes an acyclic or cyclic peroxide.

In a further subgroup, the compounds of formula (I') or (I) are acyclic with respect to  $-Z_1-Z_2-$  and symmetrically substituted, i.e.  $R_2$ ,  $R_3$  and  $R_4$  at the C-atom are the same as at the  $Z_3$ -atom, or unsymmetrically substituted, i.e. C-atom and  $Z_3$  are differently substituted. One group of the useful compounds (I') or (I) include the unsymmetrically substituted compounds.

In another subgroup, s is 0 and n is 1, or s is 1 and n is 0. Alternatively, n and s are both 1 or 0, e.g. 0.

The ring system " $R_3$  and  $R_4$  form together with said C-atom or, respectively,  $Z_3$ , wherein they are attached to, an optionally substituted, saturated, partially saturated or aromatic, mono- or polycyclic ring system of 5 to 20 carbon and, optionally, hetero ring atoms, whereby the optional hetero ring atoms are selected from N, O and/or S" can be mono-, bi- or polycyclic ring system and includes cycloalkyl, aryl and heterocyclyl ring systems, preferably of 5-16 ring atoms. Suitably said ring system is a "cycloalkyl" as defined below, suitably a saturated or partially saturated mono- or bicyclic cycloalkyl as defined above. In case  $R_3$  and  $R_4$  form a hetero ring, it is preferably "heterocyclyl" as defined below, and includes e.g. 1-4 hetero ring atoms, such as 1 or 2 O and/or, preferably, N atoms.



The definition "the two  $R_3$ 's, as given in the above formula (I), form together with the  $-(R_2R_4)C-Z_1-Z_2-Z_3((R_2),R_4)-$  moiety an optionally substituted, saturated, partially saturated or aromatic, mono- or polycyclic ring system of 5 to 20 carbon and, optionally, further hetero ring atoms, whereby the further hetero ring atoms are selected from one or two of N, O and/or S" can be mono-, bi- or polycyclic system of 5-16 ring atoms, e.g. carbon atoms, e.g. monocyclic ring of 5-12 ring atoms, and contains no further hetero atoms, or 1 or 2 further hetero atoms, e.g. N atoms.

When  $Z_3$  forms together with  $R_2$ , if present,  $R_3$  and  $R_4$ , which are attached thereto, a group  $-R'_5([Z_1-Z_2-R_6]_kZ_1-Z_2-R_5-H)_t$ , then preferably each  $R'_5$  and  $R_5$  independently is optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted cycloalkylalkyl, optionally substituted aryl, optionally substituted arylalkyl, optionally substituted heterocyclyl or optionally substituted heterocyclylalkyl; each  $R_6$  independently is optionally substituted alkyl, optionally substituted alkyl interrupted with one or more N, O and/or S, optionally substituted cycloalkyl, optionally substituted cycloalkylalkyl, optionally substituted cycloalkylalkylcycloalkyl, optionally substituted aryl, optionally substituted arylalkyl, optionally substituted arylalkylaryl, optionally substituted heterocyclyl, optionally substituted heterocyclylalkyl or optionally substituted heterocyclylalkylheterocyclyl, each  $-Z_1-Z_2-$  are  $-NR_1-NR_1-$ , preferably  $-N=N-$ ,  $t$  is 1 or 2, preferably 1, and  $k$  is as defined above. In another subgroup  $k$  is between 0-50, or between 0-10. " $t$  is 1-3" means that  $R'_5$  may be substituted with 1-3, e.g. 1 or 2, such as 1, substituent(s)  $-[Z_1-Z_2-R_6]_kZ_1-Z_2-R_5-H$ . In one preferable subgroup of the present compounds each  $R'_5$  and  $R_5$  have the same meaning or different meaning; each  $-Z_1-Z_2-$  have the same meaning and/or each  $R_6$  have the same meaning; suitably each  $R'_5$  and  $R_5$  have the same meaning or different meaning, e.g. the same meaning, each  $-Z_1-Z_2-$  have the same meaning and each  $R_6$  have the same meaning.

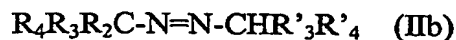
When  $Z_3$  together with  $R_2$ , if present,  $R_3$  and  $R_4$  represents a linking group  $-R_8-$  to form which is a  $R_2R_3R_4C-Z_1-Z_2-R_8-[U]_x$  which denotes a recurring structural unit of a polymer as defined above and  $x$  is 2-500, e.g. 2-200, then preferably said repeating structural unit is part of an alpha-olefin copolymer, e.g. a copolymer of ethylene with alpha- $C_3$  olefin, e.g. propylene, or of ethylene or propylene with alkyl acrylate or methacrylate, such as a copolymer of ethylene with ethylacrylate.

In a further subgroup of the invention the compounds of formula (I) have the formula (II) as defined above, preferably the compounds have a formula  $R_4R_3R_2C-N=N-CR_2R_3R_4$  (IIa).

In a still further subgroup, the compounds of formula (I') or (I), preferably (II)/(IIa), are acyclic and  $R_3$  and  $R_4$  at the same C-atom form together therewith an optionally substituted, saturated, partly saturated or aromatic, mono- or polycyclic ring system as defined above or below, and  $R_2$ ,  $R_3$  and  $R_4$  at  $Z_1$  are independently a monovalent radical as defined above, e.g. alkyl, cycloalkyl, cycloalkylalkyl, aryl, arylalkyl, whereby preferably  $R_2$  is H; or  $Z_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  form together  $-R'_5([Z_1-Z_2-R_6-]_kZ_1-Z_2-R_5-H)_t$  as defined above or below; wherein each of said groups or moieties in said groups defined for said substituents is unsubstituted or substituted independently with 1-3 "optional substituents" as defined above.

- 10 Examples of the compounds of formula (II) include bis(cycloalkylazocycloalkyl)-alkane, cycloalkylalkylazoalkane, arylalkylazoarylalkane, cycloalkylazoalkane, cycloalkylazocycloalkane, arylazoalkane and arylazoaryl compounds, preferably form bis(cycloalkylazocycloalkyl)alkane, cycloalkylazoalkane or cycloalkylazocycloalkane, wherein any of the alkyl-, aryl-, arylalkyl-, cycloalkyl- and cycloalkylalkyl is optionally substituted with 1-3 "optional substituents" as defined above.

A further suitable subgroup of compounds (I') are compounds of formula (IIb):



- wherein one or both of ( $R_3$  and  $R_4$ ) and ( $R'_3$  and  $R'_4$ ) form together with said C-atom, wherein they are attached to, an optionally substituted, saturated, partially saturated or aromatic, mono- or polycyclic ring system as defined above, preferably said ring system is selected from phenyl, mono- or bicyclic cycloalkyl of 5-16 C-atoms or mono- or bicyclic heterocyclyl of 5-16 ring atoms with 1-4 N, O and/or S atoms; or each  $R_3$  and  $R_4$  and/or each  $R'_3$  and  $R'_4$  are independently H, alkyl, alkenyl, alkynyl, aryl, arylalkyl, cycloalkyl, cycloalkylalkyl, heterocyclyl or heterocyclylalkyl, wherein the cycloalkyl and heterocyclyl as a group or part of a group is mono- or bicyclic ring with 5-16 C-atoms; or  $R_2$  is H or a bond in said ring system between said C-atom and a ring atom adjacent thereto;

- or C-atom denotes together with H,  $R'_3$  and  $R'_4$ , which are attached thereto, a group  $-R'_5([Z_1-Z_2-R_6-]_kZ_1-Z_2-R_5-H)_t$  as defined above, preferably each  $R'_5$  and  $R_5$  is independently alkyl, cycloalkyl, cycloalkylalkyl, aryl, arylalkyl, heterocyclyl or heterocyclylalkyl; each  $R_6$  independently is alkyl, alkyl interrupted with one or more N, O and/or S, cycloalkyl, cycloalkylalkyl, cycloalkylalkylcycloalkyl, aryl, arylalkyl, arylalkylaryl, heterocyclyl, heterocyclylalkyl or heterocyclylalkylheterocyclyl,

each  $-Z_1-Z_2-$  are  $-NR_1-NR_1-$ , preferably  $-N=N-$ ,  $t$  is 1 or 2, preferably 1, and  $k$  is as defined above;

- whereby each group or a moiety of a group defined as variants for  $R_3$ ,  $R_4$ ,  $R'_3$ ,  $R'_4$ ,  $R'_5$ ,  $R_5$  and  $R_6$  optionally substituted independently with 1-3, e.g. 1, of  $-OH$ ,  $-NH_2$ ,  $-COOH$ , alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkylalkyl, aryl, arylalkyl, alkyl-  
 5  $C(O)-O-$ , alkenyl- $C(O)-O-$ , such as acrylate, and/or alkyl- $O-C(O)-$ , whereby cycloalkyl and/or aryl moiety as or in said optional substituents is optionally substituted with alkyl,  $-OH$ , or alkenyl, suitably with  $CH_2=CH-$ ; as well as an oxide(s) at the azo moiety, a salt, an ester or an amide thereof.
- 10 As a further suitable subgroup are compounds of formula (IIb), wherein  $R_3$  and  $R_4$  form together with the C-atom a mono- or bicyclic cycloalkyl of 5-16 C-atoms, or  $R_2$  and  $R_3$  are H and  $R_4$  is aryl, arylalkyl, mono- or bicyclic cycloalkyl, mono- or bicyclic cycloalkylalkyl, wherein cycloalkyl as a group or as a moiety of a group has of 5-16 C-atoms, and the other C-atom forms together with H,  $R'_3$  and  $R'_4$  a group  
 15  $-R'_5([Z_1-Z_2-R_6-]_k Z_1-Z_2-R_5-H)_t$ , wherein  $R'_5$  and  $R_5$  are different or the same and selected from alkyl, alkyl interrupted with one or more O, N and/or S, aryl, arylalkyl, mono- or bicyclic cycloalkyl, mono- or bicyclic cycloalkylalkyl, wherein cycloalkyl as a group or as a moiety of a group has of 5-16 C-atoms, each  $R_6$  are the same and selected from alkyl, alkyl interrupted with one or more O, N and/or S, aryl, arylalkyl,  
 20 kylaryl, mono- or bicyclic cycloalkyl, mono- or bicyclic cycloalkylalkylcycloalkyl, wherein cycloalkyl as a group or as a moiety of a group has of 5-16 C-atoms, each  $Z_1-Z_2$  are  $-N=N-$ ,  $k$  and  $t$  are as defined above, e.g.  $k$  is 1 and  $t$  is 1; wherein each variant or a moiety of a variant is independently optionally substituted as defined under formula (IIb) above.
- 25 The invention further provides compounds of formula (IIc)



- wherein  $R_3$  and  $R_4$  form together with said C-atom, wherein they are attached to, an optionally substituted, saturated or partially saturated, mono- or polycyclic ring system as defined in claim 1, preferably said ring system is selected from mono- or bicyclic cycloalkyl of 5-16 C-atoms or mono- or bicyclic heterocyclyl of 5-16 ring atoms with 1-4 N, O and/or S atoms; or each  $R_3$  and  $R_4$  are independently alkyl, alkenyl, alkynyl, aryl, arylalkyl, cycloalkyl, cycloalkylalkyl, heterocyclyl or heterocyclylalkyl, wherein the cycloalkyl and heterocyclyl as a group or part of a group is  
 30 mono- or bicyclic ring with 5-16 ring atoms; or  $R_3$  is H and  $R_4$  is as defined above;

and  $R_2$  is H or a bond in said ring system between said C-atom and a ring atom adjacent thereto;

and C-atom denotes together with H,  $R'_3$  and  $R'_4$ , which are attached thereto, a group  $-R'_5([Z_1-Z_2-R_6-]_k Z_1-Z_2-R_5-H)_t$ , wherein each  $R'_5$  and  $R_5$  is independently alkyl, alkyl interrupted with one or more O, N and/or S, cycloalkyl, cycloalkylalkyl, arylalkyl, heterocyclyl or heterocyclylalkyl; each  $R_6$  independently is alkyl, alkyl interrupted with one or more N, O and/or S, cycloalkyl, cycloalkylalkyl, cycloalkylalkylcycloalkyl, arylalkyl, arylalkylaryl, heterocyclyl, heterocyclylalkyl or heterocyclylalkylheterocyclyl, each  $-Z_1-Z_2-$  are  $-NR_1-NR_1-$ , preferably  $-N=N-$ ,  $t$  is 1 or 2, preferably 1, and  $k$  is as defined above; whereby

each group or a moiety of a group defined as variants for  $R_3$ ,  $R_4$ ,  $R'_3$ ,  $R'_4$ ,  $R'_5$  and  $R_6$  is optionally substituted independently with 1-3, e.g. 1, of  $-OH$ ,  $-NH_2$ ,  $-COOH$ , alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkylalkyl, aryl, arylalkyl, alkyl-C(O)-O-, alkenyl-C(O)-O-, such as acrylate, and/or alkyl-O-C(O)-, whereby cycloalkyl and/or aryl moiety as or in said substituents is optionally substituted with alkenyl, such as  $CH_2=CH-$ ;

as well as an oxide(s) at the azo moiety, a salt, an ester or an amide thereof;

with the proviso that in the compounds (IIc), (a)  $R_5$  is other than methyl, and (b) when  $R'_5$  is other than triazine, then the bridge formed by  $R_6$  moiety between the two successive  $-Z_1-Z_2-$  moieties separates said two  $-Z_1-Z_2-$  moieties by 4 or more bridge atoms.

Accordingly, in a further subgroup, especially when  $R'_5$  is other than triazine, then if  $R_6$  is a chain, e.g. alkane, it is at least  $C_4$ -alkane, and if  $R_6$  is a divalent ring system, the length of bridge formed by the part of the ring is at least 4 atoms, e.g.  $C_{5-8}$ cycloalk-1,4-diyl. These compounds (IIc) are novel and form part of the invention.

Examples of compounds of formula (IIb) include:

bis(cycloalkylazocycloalkyl)alkane, arylazoalkanes, arylazoarylalkanes, arylazocycloalkanes, arylazocycloalkylalkanes, cycloalkylazocycloalkanes and alkylazoalkanes, and compounds of formula (IIc) include bis(cycloalkylazocycloalkyl)alkane; each optionally substituted e.g. with 1-3 substituent(s) as defined above, such as with a substituent  $R''=$  alkenyl, e.g.  $CH_2=CH-$ ,  $NH_2$ ,  $-OH$ ,  $-COOH$ ,  $-O-C(O)-CH=CH_2$  or  $-C(O)O$ -alkyl, non-limiting examples being  $R''-(CH_2)_{2-20}-N=N-C_{5-8}$ -cycloalkyl, wherein the cycloalkyl is suitably a saturated monocycle and  $R''$  as de-

defined above. Representatives of the compounds (IIb) and (IIc) are cyclohexylazo-n-hexadecyl-diazene and 4,4'-bis(cyclohexylazo-cyclohexyl)methane.

In a further suitable subgroup of the present compounds or e.g. in compounds of formula (I'), (I), (IIa), (IIb) or (IIc): (i) at one of the C-atom and Z<sub>3</sub>, as depicted in  
 5 formula (I'), R<sub>2</sub>, R<sub>3</sub> and/or R<sub>4</sub> is a monovalent radical selected from optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted cycloalkylalkyl or optionally substituted heterocyclyl(O)<sub>s</sub>(alkyl)<sub>n</sub> as defined above, whereby each said ring as a group or as part of a group is saturated or partially saturated, such as saturated, ring system; and any remaining R<sub>2</sub>, R<sub>3</sub> or R<sub>4</sub> is a group or forms a  
 10 group other than aryl or heteroaryl; preferably one of R<sub>3</sub> and R<sub>4</sub> is optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted cycloalkylalkyl or optionally substituted heterocyclyl(O)<sub>s</sub>(alkyl)<sub>n</sub> as defined above, whereby each said ring as a group or as part of a group is saturated or partially saturated, such as saturated, ring system, and the other of R<sub>3</sub> and R<sub>4</sub> is alkyl or H, e.g. H, and R<sub>2</sub>, if  
 15 present, is a bond or H, e.g. H; or

(ii) at one of the C-atom and Z<sub>3</sub>, as depicted in the formula (I'), R<sub>3</sub> and R<sub>4</sub> form together with said C-atom or, respectively, Z<sub>3</sub>, wherein they are attached to, an optionally substituted, saturated or partially saturated ring system, such as saturated or partially saturated cycloalkyl or heterocyclyl, suitably cycloalkyl, each of which  
 20 may be optionally substituted, and R<sub>2</sub>, if present, is a bond, H or a monovalent radical as defined above other than aryl, e.g. a bond or H, such as H; preferably R<sub>3</sub> and R<sub>4</sub> form together with said C-atom; or

(iii) Z<sub>3</sub>-atom (as depicted in formula (I')) forms together with R<sub>2</sub>, if present, R<sub>3</sub> and R<sub>4</sub> a group -R'<sub>5</sub>([Z<sub>1</sub>-Z<sub>2</sub>-R<sub>6</sub>]<sub>k</sub>Z<sub>1</sub>-Z<sub>2</sub>-R<sub>5</sub>-H)<sub>t</sub>, each R'<sub>5</sub> and R<sub>5</sub> is independently optionally substituted alkyl, optionally substituted alkyl interrupted with one or more N, O  
 25 and/or S, optionally substituted cycloalkyl, optionally substituted cycloalkylalkyl, optionally substituted cycloalkylalkylcycloalkyl, optionally substituted, saturated or partially saturated heterocyclyl, optionally substituted heterocyclylalkyl or optionally substituted heterocyclylalkylheterocyclyl, whereby each said ring as a group or  
 30 as part of a group is saturated or partially saturated, such as saturated, ring system; each R<sub>6</sub> independently has a meaning as given for R'<sub>5</sub> and R<sub>5</sub> herein, each Z<sub>1</sub> and Z<sub>2</sub> are -N=N-, and k and t are as defined above, suitably t is 1 or 2, preferably 1;

the "optional substituents" being as defined above;

or both the C-atom and  $Z_3$  are substituted as defined in one of (i)-(iii). Suitably the optional substituents in any of the above defined groups or in a moiety of said groups is as defined above except an aromatic ring, such as aryl and heteroaryl.

In one alternative subgroup of the invention  $R_2$ - $R_4$  at the C-atom as depicted in formula (I') bear or form no aromatic ring systems, such as aryl and heteroaryl. In another subgroup both at the C-atom and at  $Z_3$ , as depicted in formula (I'),  $R_2$ - $R_4$  bear or form no aromatic ring systems, such as aryl and heteroaryl.

The terms employed above or below under any of the given formulae and under lists defining separately a substituent or a subgroup, mean in general as follows, unless otherwise stated: The term "alkyl", "alkenyl" and "alkynyl" as a group or as part of another group (such as in "arylalkyl") include both straight and branched chain radicals of up to 50 carbon atoms, preferably up to 20 carbon atoms. In certain embodiments and, particularly, in case "alkyl", "alkenyl" and "alkynyl" are as part of another group, as "optional substituent(s)" for a given group or as  $R_8$ , they suitably contain up to 9, preferably up to 6 or 4, e.g. 1 or 2, carbon atoms. Furthermore, "Alkenyl" and "alkynyl" may have one or more double or, resp., triple bonds, e.g. one double or, resp., one triple bond, e.g. radical of 1-alkenyl. "Alkyl interrupted with a hetero atom" may have a one or more, suitably 1-5, such as 1, hetero atom. "Cycloalkyl" as a group or as part of another group is saturated or partially saturated mono-, bi-, or polycyclic carbocycle of 3-16, preferably of 5-12 carbon atoms, suitably saturated monocyclic ring, such as cyclopentyl, cyclohexyl, cycloheptyl or cyclooctyl, or saturated bicyclic ring, such as a "monocycle" as defined above which is fused with a saturated ring moiety of 5 to 8 ring atoms, e.g. with cyclohexyl moiety. Alternatively, partially saturated "cycloalkyl" is as defined above for saturated cycloalkyl except that it contains e.g. one to two double or, resp., triple bond(s) in the ring structure thereof, whereby in case of a bicycle also systems wherein a saturated monocycle is fused with an aromatic ring moiety, e.g. benzo moiety, are covered. "Aryl" is phenyl or naphthyl, preferably phenyl. "Heterocyclyl" as used alone or as part of "heterocyclyl(O)<sub>s</sub>(alkyl)<sub>n</sub>" has 5 to 16 ring atoms with one to four heteroatoms selected from N, O and/or S and can be mono-, bi-, or polycyclic, e.g. 5-6 membered monocyclic ring. Said heterocyclyl covers saturated or partially saturated heterocyclyls and aromatic heterocyclyls, i.e. heteroaryls.

In FR use the compound of the invention can be added to the polymeric substrate alone or as a mixture of one or more compounds (I'). The amount is chosen in a manner known in the art so that an industrially acceptable flame retarding property is provided to the polymeric substrate. Naturally the "effective amount" varies de-

pending i.e. on the used polymeric substrate and use of application of the obtained flame retarded polymeric substrate and can be determined by a skilled person. As an example, amounts from 0.1-20 weight-% based on the polymeric substrate, preferably 0.1-10 wt-%.

- 5 The present invention further provides a FR composition, comprising a polymeric substrate and an effective amount of a compound of formula (I'), (I) or (II)/(IIa)/(IIb)/(IIc), or any mixture thereof.

Furthermore, the compounds of the invention may be used as FR synergists in a mixture with one or more further FR's. Such mixtures are also covered by the composition of the invention. It is possible, if desired, to combine the specific compounds (I) or (IIb)/(IIc) with halogenated FR's, but preferably any further flame retardant used in the composition of the invention is a non-halogenated FR. Examples of the usable further FR's include NOR-hindered amines (see WO99/004500), aluminium and boron compounds, such as aluminium trihydrate, magnesium hydroxide, intumescent systems, e.g. expandable graphite.

If synergistic mixtures with the other compounds (I') or with further FR's other than compounds (I') as described above are used, then naturally lower amounts of a compound (I') are needed to achieve an effective FR effect. The term "effective amount" includes also the lower amounts used in such synergistic mixtures.

- 20 The polymeric substrates can be chosen from a wide variety of polymers including polyolefins, such as thermoplastic polyolefins, aromatic polyolefins, e.g. polystyrenes, high impact polystyrene or ABS, polycarbonates, PVC, or polysaccharide based polymers, preferably polypropylene, polyethylene, thermoplastic polyolefin, ABS, polycarbonate and high impact polystyrene, as well as any copolymers, block polymers, graft polymers or any mixtures or blends thereof.

In the present FR method the present compound of the invention is/are added to the polymeric substrate and the admixture is further processed to a product of an end application. The addition can be effected at any stage, e.g. during the polymerisation process of the polymer or during compounding. Alternatively, the compound of the invention can be incorporated to the backbone of a polymeric substrate or of part of a polymeric substrate, or of one or more polymeric component(s) of the polymeric substrate. Grafting can be effected in a manner known in the art using compounds (I')/(I) which comprise functionalities in the substituents  $R_2$ - $R_4$ , e.g. double or triple bond(s), OH,  $-NH_2$ ,  $-COOH$ , which are reactive with the function-

alities of the polymeric material. Thus the compounds (I')/(I) and their use as FR cover also such embodiments, wherein they are incorporated chemically to a part or all of the polymeric material ("functionalised/grafted" polymeric material) of the polymeric substrate.

- 5 If polymeric substrate comprises two or more different polymeric materials, the compound(s) (I')/(I) can be combined by mixing or grafting with one of the materials, and the rest be added to the obtained first composition.

The term "A flame retardant composition" used herein covers any bulk polymeric material, e.g. pellets, which is further processed to end products as well as the final applications, i.e. the end products. The flame retardant of the invention may thus be  
10 used i.a. for producing cables, fibres, textiles, films, laminates, polymer foams, electronic components etc.

Conventional additives other than flame retardants can also be added to the flame retardant composition of the invention in a conventional manner. Examples include  
15 UV absorbers, light stabilisers, antioxidants, colorants etc.

The compounds of the invention can be prepared accordingly or analogously to wide variety of synthetic routes disclosed in the prior art. Some of the various methods are described below for certain preferred subgroups of the compounds.

Compounds (I')/(I) of interest include symmetrical azoalkanes. The symmetrical  
20 azoalkanes can be obtained by reacting sulfonyl chloride with at least 2 equivalents of the suitable alkylamine, followed by oxidation of the obtained N,N'-dialkylsulfamide to the azoalkane. Suitable oxidizing agent include alkaline hypochlorite.

Other compounds (I')/(I) of interest are unsymmetrical, optionally functionalised,  
25 azo compounds. These chemicals can be prepared by the skilled in the art by reacting an optionally functionalised amine with an optionally functionalised N-substituted sulfamoyl chloride, and oxidizing the obtained sulfamide derivative to yield the desired unsymmetrical, optionally functionalised, azo compound.

Azoalkanes can also be prepared by oxidation of the N, N'-dialkylhydrazine equivalent  
30 with copper (II) chloride, copper(II) acetate or mercury(II) oxide for example. When the azo functionality is part of a ring, the azo compound of interest is obtained from the oxidation of the cyclic hydrazine equivalent.



Another group of compounds (I')/(I) of interest are hydrazines. Acyclic and cyclic hydrazines may be prepared by alkylation of N,N'-diformylhydrazine, diacetyl diazene, bis(2-methyl-1-oxopropyl) diazene or di(ar)alkyl azodicarboxylate for instance, and subsequent hydrolysis. A possible alternative to the synthesis of hydrazines is via the reduction of the corresponding azine, using a reducing agent such as lithium aluminum hydride or using catalytic hydrogenation techniques.

Another group of compounds (I')/(I) of interest are cyclic or acyclic hydrazones. Cyclic or acyclic hydrazones can be obtained from the condensation of a suitable carbonyl-containing compound such as aldehyde or ketone with a monosubstituted hydrazine. Hydrazones of particular interest are the tautomer equivalents to the azo compounds of interest.

Another group of compounds (I')/(I) of interest consists of azines. Azines are prepared from the condensation reaction of identical or different carbonyl-containing compound such as aldehyde or ketone with hydrazine.

Another group of compounds (I')/(I) of interest are triazenes. Alkylation of azides with nucleophiles such as grignard reagents yields 1,3-disubstituted triazenes. 1,1,3-trisubstituted triazenes are obtained from further alkylation of 1,3-disubstituted triazenes under alkaline conditions.

Another group of compounds (I')/(I) of interest is constituted of the oxides(s) of azo compounds, which includes diazene-N,N'-dioxide and diazene-N-oxide derivatives of the azo compounds. These compounds can be synthesized by treatment of the corresponding azo chemicals with an oxidative agent such as peroxy acids or peroxides.

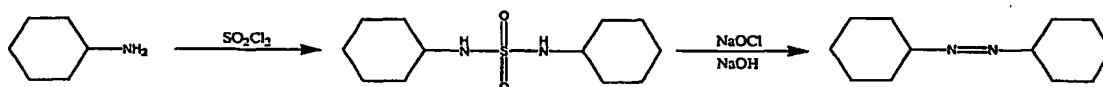
Another group of compounds (I')/(I) of interest is based on organic peroxides. Production of symmetrical or unsymmetrical organic peroxides can be prepared by the skilled in the Art via alkylation of hydroperoxides with for instance alcohols, olefins or halides. Of particular interest are the acyclic symmetrical or unsymmetrical di(ar)alkylperoxides, possibly substituted.

## Examples

The used reagents and starting material were commercially available or can be prepared with the methods described in the literature.

### Example 1

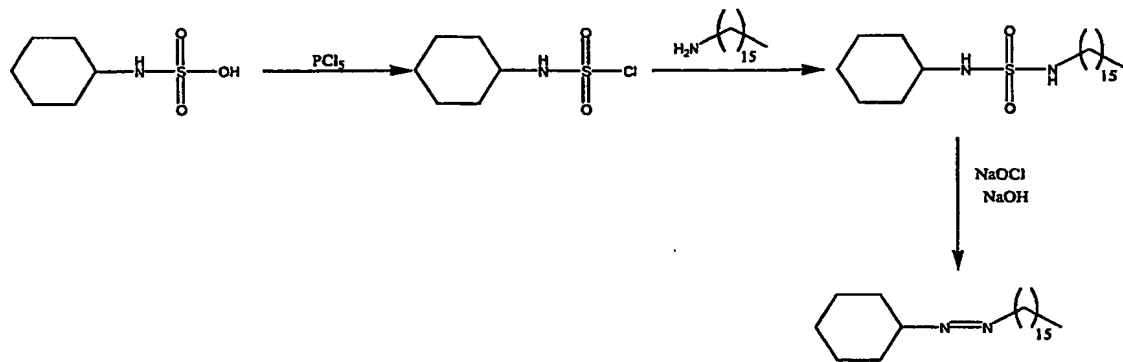
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Under a nitrogen atmosphere, a solution of 98.5% sulfonyl chloride (10.0mL, 121mmol) in 40 mL of dichloromethane was added dropwise at 0°C to a solution of cyclohexylamine (30.0g, 303mmol) and triethylamine (84mL, 606mmol) in 150mL of dichloromethane. The reaction mixture was stirred 4 hours at 0°C, neutralized with water, and diluted in dichloromethane (300mL). The organic components were successively washed with diluted hydrochloric aqueous solution, NaHCO<sub>3</sub> aqueous solution and brine, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated under reduced pressure. The residue was suspended in ether, filtered through Büchner, and the precipitate washed two times with 100ml of ether to yield white crystals of N,N'-bis(cyclohexyl)sulfamide (14.0g, 45%).

10g of the N,N'-bis(cyclohexyl)sulfamide (38mmol) were slowly added at 0°C to a solution of 10% aqueous NaOCl (114g, 153mmol) and NaOH (6.2g, 155mmol). The reaction mixture was stirred 3 hours at 60°C, cooled down to room temperature and diluted in 500mL of dichloromethane. The organic components were successively washed with water and an aqueous sodium bisulfite solution, dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated under reduced pressure. The residue was purified by chromatography (silica gel; light petroleum ether/ ethyl acetate 20/1) to yield AA3 as yellow-white crystals (6.5g, 87%).

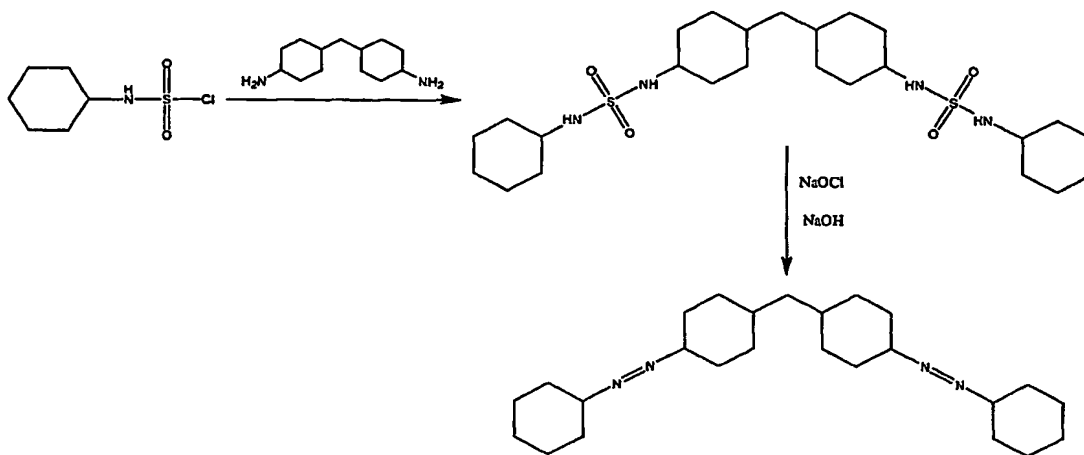
<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 3.24 (m, 2H), 1.85-1.79 (m, 4H), 1.69-1.60 (m, 10H), 1.37-1.20 (m, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub> δ): 75.9; 30.7; 25.5; 24.3. Exact mass calcd for C<sub>12</sub>H<sub>22</sub>N<sub>2</sub> requires m/z 194.1783, found 194.1784.

**Example 2**

- Under a nitrogen atmosphere, a solution of N-cyclohexylsulfamic acid (50g, 279mmol) and  $\text{PCl}_5$  (58.1g, 279mmol) in 150mL of toluene was very gently warmed up to  $100^\circ\text{C}$  and maintained at that temperature for 1 hour. Distillation of the solution yielded N-cyclohexylsulfamoyl chloride as a colorless solid (45.5g, 82%).
- A solution of 13.6g of the cyclohexylsulfamoyl chloride (69mmol) in 100mL of dichloromethane was added under argon atmosphere to a solution of 1-hexadecylamine (19.9g, 82mmol) and triethylamine (47.5mL, 340mmol) in 300mL of dichloromethane. The reaction mixture was stirred 5 hours at  $0^\circ\text{C}$ , neutralized with an aqueous  $\text{Na}_2\text{CO}_3$  solution and concentrated under reduced pressure. The residue was taken up in dichloromethane (800mL). The organic components were successively washed with diluted hydrochloric aqueous solution,  $\text{NaHCO}_3$  aqueous solution and brine, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated under reduced pressure. The residue was suspended in ether, filtered through Büchner, and the precipitate was washed two times with 100ml of ether to yield a white powder of N-cyclohexyl-N'-hexadecylsulfamide (21.8g, 79%).
- The N-cyclohexyl-N'-hexadecylsulfamide was oxidized to the cyclohexylazo-n-hexadecyl-diazenes using basic bleach in a procedure similar to the one described above for the synthesis of azocyclohexane from N,N'-bis(cyclohexyl)sulfamide.
- The cyclohexylazo-n-hexadecyl-diazenes product is obtained as a yellow solid of low melting point, in a yield of 77% from 20.0g of N-cyclohexyl-N'-hexadecylsulfamide (50mmol).

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 3.70 (t,  $^3J=7.2$  Hz, 2H); 3.30 (tt,  $^3J=5.2$  Hz,  $^3J=5.1$  Hz, 1H); 1.85-1.60 (m, 9H); 1.30-1.20 (m, 29H); 0.85 (t,  $^3J=7$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$   $\delta$ ): 76.0; 69.0; 31.9; 30.6; 29.7 (br.); 29.6; 29.6; 29.5; 29.4; 27.6; 27.2; 25.6; 24.3; 22.7; 14.0. Exact mass calcd for  $\text{C}_{22}\text{H}_{44}\text{N}_2$  requires  $m/z$  336.3504, found 336.3503.

### 5 Example 3



4,4'-bis(cyclohexylazocyclohexyl)methane was prepared from cyclohexylsulfamoyl chloride and 4,4'-diaminodicyclohexylmethane following a similar multistep synthesis as the one used for the synthesis of cyclohexylazo-n-hexadecyl-diazene, in an overall yield of 26%.

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ ): 3.1-3.3 (m, 4H); 0.90-1.85 (m, 40H). Exact mass calcd for  $\text{C}_{25}\text{H}_{44}\text{N}_4$  requires  $m/z$  400.3566, found 400.3573.

### Comparison test: Flame Retardancy Testing

The FR efficacy of the compounds of the invention was tested with a commercially available NOR-hindered amine compound Ciba® FLAMESTAB® NOR 116 (reaction product of N,N'-ethane-1,2-diylbis(1,3-propanediamine), cyclohexane, peroxidized 4-butylamino-2,2,6,6-tetramethylpiperidine and 2,4,6-trichloro-1,3,5-triazine, available from Ciba), which represents the closest prior art: it is non-halogenated and known to be effective alone as FR and can be used in place of conventional halogenated FR's.

Polypropylene was blended with 0.1% by weight of calcium stearate, 0.2% of CIBA® Irganox® B 501 and 0%, 0.25% or 0.5% of the test FR's. The blends were melt processed into fibres, spun into socks and subsequently compression molded into thin films. The FR efficacy was tested according to the known DIN 4102 Part 1  
 5 Classification B2 test method.

Table 1: results of a DIN 4102 test, face ignition, (230 x 90mm samples)

Formulation	Average damaged area (cm <sup>2</sup> )	Total burning time (sec.)
Blank	184	32
0.25% Flamestab NOR 116	55	20
0.50% Flamestab NOR 116	38	21
0.25% example 3	28	13
0.50% example 3	21	8
0.25% example 2	39	18
0.50% example 2	31	13
0.25% example 1	39	16
0.50% example 1	22	10

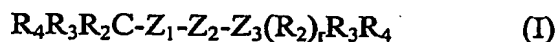
Table 2: DIN 4102 test, edge ignition (190 x 90mm samples)

Formulation	Average damaged length (mm)	Total burning time (sec.)
Blank	190	30.4
0.25% Flamestab NOR 116	47	11.0
0.50% Flamestab NOR 116	46	12.6
0.25% example 3	37	10.6
0.50% example 3	45	11.8
0.25% example 2	54	15.8
0.50% example 2	45	12.6
0.25% example 1	41	11.6
0.50% example 1	41	9.8

From these experiments, it is clear that the compounds of the invention provide fire retardancy and self-extinguishing properties to polypropylene samples at very low concentrations.

## Claims

### 1. Use of a compound of formula (I)



- 5 wherein  $Z_1$  and  $Z_2$  are both  $NR_1$  and  $Z_3$  is C or N; or  $Z_1$  and  $Z_2$  are both O and  $Z_3$  is C;  $r$  is 0, when  $Z_3$  is N, and  $r$  is 1, when  $Z_3$  is C;

the two  $R_1$ 's form together a bond or each  $R_1$  is independently H or forms a bond together with  $R_2$  present at the adjacent C-atom or, respectively,  $Z_3$ ;

- 10 each  $R_2$  independently forms a bond or is a monovalent radical as defined for  $R_3$  and  $R_4$  below;

- each  $R_3$  and  $R_4$  is independently a monovalent radical selected from H, optionally substituted alkyl, optionally substituted alkyl interrupted with one or more O, N and/or S atom(s), optionally substituted cycloalkyl, optionally substituted cycloalkylalkyl, optionally substituted aryl, optionally substituted arylalkyl, optionally substituted alkoxy(alkyl)<sub>n</sub>, optionally substituted aryloxy(alkyl)<sub>n</sub>, optionally substituted arylalkyloxy(alkyl)<sub>n</sub>, optionally substituted alkenyl, optionally substituted alkenyloxy(alkyl)<sub>n</sub>, optionally substituted alkynyl, optionally substituted alkynyloxy(alkyl)<sub>n</sub>, optionally substituted heterocyclyl(O)<sub>s</sub>(alkyl)<sub>n</sub> with one to four heteroatoms selected independently from N, O and S;  $R-Y-C(O)-(alkyl)_n$  or  $R-C(O)-Y-(alkyl)_n$ , wherein each R independently is H, alkyl, alkenyl, cycloalkyl, aryl or heterocyclyl as defined above, each of which is optionally substituted, Y is O or NH;
- 15
- 20

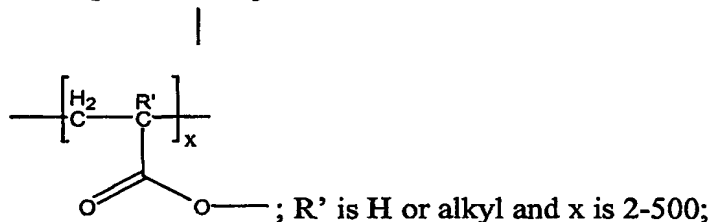
- or at one or both of the C-atom and  $Z_3$ , as given in the above formula (I),  $R_3$  and  $R_4$  form together with said C-atom or, respectively,  $Z_3$ , wherein they are attached to, an optionally substituted, saturated, partially saturated or aromatic, mono- or poly-
- 25 cyclic ring system of 5 to 20 carbon and, optionally, hetero ring atoms, whereby the optional hetero ring atoms are selected from N, O and/or S; and  $R_2$  is a monovalent radical as defined for  $R_3$  and  $R_4$  above, or forms a bond between the C-atom and  $Z_1$  or, respectively, between  $Z_3$  and  $Z_2$ , or forms a bond in the ring system formed by  $R_3$  and  $R_4$  between said C-atom or, respectively,  $Z_3$ , and a ring atom adjacent
- 30 thereto;

each  $s$  and  $n$  is independently 0 or 1;

or  $Z_3$  forms together with  $R_2$ , if present,  $R_3$  and  $R_4$ , which are attached thereto, a group  $-R'_5([Z_1-Z_2-R_6-]_k Z_1-Z_2-R_5-H)_t$ , wherein each  $R'_5$  and  $R_5$  is independently optionally substituted alkyl, optionally substituted alkyl interrupted with one or more N, O and/or S, optionally substituted cycloalkyl, optionally substituted cycloalkylalkyl, optionally substituted cycloalkylalkylcycloalkyl, optionally substituted aryl, optionally substituted arylalkyl, optionally substituted arylalkylaryl, optionally substituted heterocyclyl, optionally substituted heterocyclylalkyl or optionally substituted heterocyclylalkylheterocyclyl, each  $R_6$  independently has a meaning as given for  $R'_5$  and  $R_5$  above,  $Z_1$  and  $Z_2$  are each independently as defined above,  $t$  is 1-3 and  $k$  is chosen so that the molecular weight of the resulting compound of formula (I) is within 200 to 10000 g/mol;

or  $Z_3$  together with  $R_2$ , if present,  $R_3$  and  $R_4$ , which are attached thereto, represent a linking group  $-R_8-$  to form  $R_2R_3R_4C-Z_1-Z_2-R_8-[U]_x$  which denotes a recurring structural unit of a polymer, wherein  $R_8$  is a linking bond or alkyl, cycloalkyl, heterocyclyl or aryl;

$U$  is a  $[-CH_2-CR'-]_x$ , or



or the two  $R_3$ 's, as given in the above formula (I), form together with the  $-(R_2R_4)C-Z_1-Z_2-Z_3((R_2)_rR_4)-$  moiety an optionally substituted, saturated, partially saturated or aromatic, mono- or polycyclic ring system of 5 to 20 carbon and; optionally, further hetero ring atoms, whereby the further hetero ring atoms are selected from one or two of N, O and/or S; and wherein  $Z_1$  to  $Z_3$ ,  $r$  and  $R_2$  to  $R_4$  are as defined above;

(a) with the proviso that in the compound of formula (I) at least at one of the C-atom and  $Z_3$ , as depicted in the above formula (I),  $R_3$  and  $R_4$  are independently other than H and  $R_2$  is H or a bond; and

(b) the compound of formula (I) is selected from the following compounds of formulae (II)-(IV):

a compound of formula (II)





wherein the two  $R_1$ 's form together a bond, or each  $R_1$  independently is H or forms a bond together with  $R_2$  present at the adjacent C-atom as defined above;

a compound of formula (III)



5 wherein the two  $R_1$ 's form together a bond; or

a compound of formula (IV)



wherein in the above formulae (II)-(IV)  $R_1$  to  $R_4$  are defined as above;

10 as well as use of an oxide of N as  $Z_1$ - $Z_3$ , a salt, an ester or an amide thereof, or of a mixture of two or more compounds of formula (I) as defined above;

as a flame retardant for a polymeric substrate.

2. Use of claim 1, wherein both at the C-atom and at the  $Z_3$ -atom  $R_3$  and  $R_4$  are other than H and  $R_2$  is H or a bond.

15 3. Use of claim 1 or 2, wherein the compound (I) is acyclic and  $-Z_1$ - $Z_2$ - is symmetrically substituted.

4. Use of claim 1 or 2, wherein the compound (I) is acyclic and  $-Z_1$ - $Z_2$ - is unsymmetrically substituted.

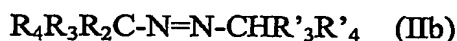
5. Use of any of the preceding claims, wherein the compound of formula (I) is the compound of formula (II) as defined in claim 1, preferably a compound of formula  
20  $R_4R_3R_2C-N=N-CR_2R_3R_4$  (IIa).

6. Use of any of the preceding claims, wherein the compound of formula (II) is acyclic and  $R_3$  and  $R_4$  at the same C-atom form together therewith an optionally substituted, saturated, partly saturated or aromatic, mono- or polycyclic ring system as defined in claim 1, preferably said rings are selected from cycloalkyl or aryl  
25 which is unsubstituted or substituted with 1-3, e.g. 1, of  $-OH$ ,  $-NH_2$ ,  $-COOH$ , alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkylalkyl, aryl, arylalkyl, alkyl-C(O)-O-, alkenyl-C(O)-O-, such as acrylate, and/or alkyl-O-C(O)-, whereby cycloalkyl and/or aryl moiety as or in said substituents is optionally substituted with alkenyl, such as  $CH_2=CH-$ .

7. Use of any of the preceding claims, wherein  $Z_3$  forms together with  $R_2$ ,  $R_3$  and  $R_4$ , which are attached thereto, a group  $-R'_5([Z_1-Z_2-R_6-]_k Z_1-Z_2-R_5-H)_t$  as defined in claim 1, preferably each  $R'_5$  and  $R_5$  is independently optionally substituted alkyl, optionally substituted cycloalkyl, optionally substituted cycloalkylalkyl, optionally substituted aryl, optionally substituted arylalkyl, optionally substituted heterocyclyl or optionally substituted heterocyclylalkyl; each  $R_6$  independently is optionally substituted alkyl, optionally substituted alkyl interrupted with one or more N, O and/or S, optionally substituted cycloalkyl, optionally substituted cycloalkylalkyl, optionally substituted cycloalkylalkylcycloalkyl, optionally substituted aryl, optionally substituted arylalkyl, optionally substituted arylalkylaryl, optionally substituted heterocyclyl, optionally substituted heterocyclylalkyl or optionally substituted heterocyclylalkylheterocyclyl, each  $-Z_1-Z_2-$  are  $-NR_1-NR_1-$ , preferably  $-N=N-$ ,  $t$  is 1 or 2, preferably 1, and  $k$  is as defined in claim 1.

8. Use of any of the preceding claims, wherein the compound of formula (II) is selected from bis(cycloalkylazocycloalkyl)alkane, cycloalkylalkylazoalkane, arylalkylazoarylalkane, cycloalkylazoalkane, cycloalkylazocycloalkane, arylazoalkane and arylazoaryl compounds, preferably from bis(cycloalkylazocycloalkyl)alkane, cycloalkylazoalkane or cycloalkylazocycloalkane, whereby any of the alkyl-, aryl-, arylalkyl-, cycloalkyl- and cycloalkylalkyl is optionally substituted with 1-3 substituents; for example azocyclohexane, cyclohexylazo-n-hexadecyl-diazene or 4,4'-bis(cyclohexylazo-cyclohexyl)methane.

9. Use of any of the preceding claims, wherein the compound of formula (I) is a compound of formula (IIb)



wherein one or both of ( $R_3$  and  $R_4$ ) and ( $R'_3$  and  $R'_4$ ) form together with said C-atom, wherein they are attached to, an optionally substituted, saturated, partially saturated or aromatic, mono- or polycyclic ring system as defined in claim 1, preferably said ring system is selected from phenyl, mono- or bicyclic cycloalkyl of 5-16 C-atoms or mono- or bicyclic heterocyclyl of 5-16 ring atoms with 1-4 N, O and/or S atoms; or each  $R_3$  and  $R_4$  and/or each  $R'_3$  and  $R'_4$  are independently H, alkyl, alkenyl, alkynyl, aryl, arylalkyl, cycloalkyl, cycloalkylalkyl, heterocyclyl or heterocyclylalkyl, wherein the cycloalkyl and heterocyclyl as a group or part of a group is mono- or bicyclic ring with 5-16 ring atoms; and  $R_2$  is H or a bond in said ring system between said C-atom and a ring atom adjacent thereto;

or C-atom denotes together with H, R'<sub>3</sub> and R'<sub>4</sub>, which are attached thereto, a group -R'<sub>5</sub>[(Z<sub>1</sub>-Z<sub>2</sub>-R<sub>6</sub>)]<sub>k</sub>Z<sub>1</sub>-Z<sub>2</sub>-R<sub>5</sub>-H, as defined claim 1, preferably each R'<sub>5</sub> and R<sub>5</sub> is independently alkyl, cycloalkyl, cycloalkylalkyl, aryl, arylalkyl, heterocyclyl or heterocyclylalkyl; each R<sub>6</sub> independently is alkyl, alkyl interrupted with one or  
 5 more N, O and/or S, cycloalkyl, cycloalkylalkyl, cycloalkylalkylcycloalkyl, aryl, arylalkyl, arylalkylaryl, heterocyclyl, heterocyclylalkyl or heterocyclylalkylheterocyclyl, each -Z<sub>1</sub>-Z<sub>2</sub>- are -NR<sub>1</sub>-NR<sub>1</sub>-, preferably -N=N-, t is 1 or 2, preferably 1, and k is as defined in claim 1; whereby

each group or a moiety of a group defined as variants for R<sub>3</sub>, R<sub>4</sub>, R'<sub>3</sub>, R'<sub>4</sub>, R'<sub>5</sub>, R<sub>5</sub>  
 10 and R<sub>6</sub> optionally substituted independently with 1-3, e.g. 1, of -OH, -NH<sub>2</sub>, -COOH, alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkylalkyl, aryl, arylalkyl, alkyl-C(O)-O-, alkenyl-C(O)-O-, such as acrylate, and/or alkyl-O-C(O)-, whereby cycloalkyl and/or aryl moiety as or in said substituents is optionally substituted with alkenyl, such as CH<sub>2</sub>=CH-;

15 as well as an oxide(s) at the azo moiety, a salt, an ester or an amide thereof.

10. A compound of formula (IIc)



wherein R<sub>3</sub> and R<sub>4</sub> form together with said C-atom, wherein they are attached to, an optionally substituted, saturated or partially saturated, mono- or polycyclic ring system as defined in claim 1, preferably said ring system is selected from mono- or bi-  
 20 cyclic cycloalkyl of 5-16 C-atoms or mono- or bicyclic heterocyclyl of 5-16 ring atoms with 1-4 N, O and/or S atoms; or each R<sub>3</sub> and R<sub>4</sub> are independently alkyl, alkenyl, alkynyl, aryl, arylalkyl, cycloalkyl, cycloalkylalkyl, heterocyclyl or heterocyclylalkyl, wherein the cycloalkyl and heterocyclyl as a group or part of a group is  
 25 mono- or bicyclic ring with 5-16 ring atoms; or R<sub>3</sub> is H and R<sub>4</sub> is as defined above; and R<sub>2</sub> is H or a bond in said ring system between said C-atom and a ring atom adjacent thereto;

and C-atom denotes together with H, R'<sub>3</sub> and R'<sub>4</sub>, which are attached thereto, a group -R'<sub>5</sub>[(Z<sub>1</sub>-Z<sub>2</sub>-R<sub>6</sub>)]<sub>k</sub>Z<sub>1</sub>-Z<sub>2</sub>-R<sub>5</sub>-H, wherein each R'<sub>5</sub> and R<sub>5</sub> is independently al-  
 30 kyl, alkyl interrupted with one or more O, N and/or S, cycloalkyl, cycloalkylalkyl, arylalkyl, heterocyclyl or heterocyclylalkyl; each R<sub>6</sub> independently is alkyl, alkyl interrupted with one or more N, O and/or S, cycloalkyl, cycloalkylalkyl, cycloalkylalkylcycloalkyl, arylalkyl, arylalkylaryl, heterocyclyl, heterocyclylalkyl or hetero-

cyclylalkylheterocyclyl, each  $-Z_1-Z_2-$  are  $-NR_1-NR_1-$ , preferably  $-N=N-$ ,  $t$  is 1 or 2, preferably 1, and  $k$  is as defined in claim 1; whereby

- each group or a moiety of a group defined as variants for  $R_3$ ,  $R_4$ ,  $R'_3$ ,  $R'_4$ ,  $R'_5$ ,  $R_5$  and  $R_6$  is optionally substituted independently with 1-3, e.g. 1, of  $-OH$ ,  $-NH_2$ ,  $-COOH$ , alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkylalkyl, aryl, arylalkyl, alkyl- $C(O)-O-$ , alkenyl- $C(O)-O-$ , such as acrylate, and/or alkyl- $O-C(O)-$ , whereby cycloalkyl and/or aryl moiety as or in said substituents is optionally substituted with alkenyl, such as  $CH_2=CH-$ ;

as well as an oxide(s) at the azo moiety, a salt, an ester or an amide thereof;

- 10 with the proviso that in the compounds (IIc), (a)  $R_5$  is other than methyl, and (b) when  $R'_5$  is other than triazine, then the bridge formed by  $R_6$  moiety between the two successive  $-Z_1-Z_2-$  moieties separates said two  $-Z_1-Z_2-$  moieties by 4 or more bridge atoms.

11. A compound of claim 10, which is 4,4'-bis(cyclohexylazo-cyclohexyl)methane.

- 15 12. A flame retardant composition, which comprises

(a) a polymeric substrate, and

(b) an effective amount of a compound of formula (I) or a compound of formula (IIb) or (IIc) as defined in any of claims 1-11 or a mixture thereof.

13. A method of flame retarding a polymeric substrate, wherein an effective flame  
20 retarding amount of the compound of formula (I) or a compound of formula (IIb) or (IIc) as defined in claim 1-11 or a mixture thereof is added to the polymeric substrate.

14. A flame retardant composition, which comprises

(a) a polymeric substrate, and

- 25 (b) an effective amount of a compound of formula (I')



wherein  $Z_1$  and  $Z_2$  are both  $NR_1$  and  $Z_3$  is C or N; or  $Z_1$  and  $Z_2$  are both O and  $Z_3$  is C;  $r$  is 0, when  $Z_3$  is N, and  $r$  is 1, when  $Z_3$  is C;

the two  $R_1$ 's form together a bond or each  $R_1$  is independently H or forms a bond together with  $R_2$  present at the adjacent C-atom or, respectively,  $Z_3$ ;

each  $R_2$  independently forms a bond or is a monovalent radical as defined for  $R_3$  and  $R_4$  below;

- 5 each  $R_3$  and  $R_4$  is independently a monovalent radical selected from H, optionally substituted alkyl, optionally substituted alkyl interrupted with one or more O, N and/or S atom(s), optionally substituted cycloalkyl, optionally substituted cycloalkylalkyl, optionally substituted aryl, optionally substituted arylalkyl, optionally substituted alkoxy(alkyl)<sub>n</sub>, optionally substituted aryloxy(alkyl)<sub>n</sub>,  
 10 optionally substituted arylalkyloxy(alkyl)<sub>n</sub>, optionally substituted alkenyl, optionally substituted alkenyloxy(alkyl)<sub>n</sub>, optionally substituted alkynyl, optionally substituted alkynyloxy(alkyl)<sub>n</sub>, optionally substituted heterocyclyl(O)<sub>s</sub>(alkyl)<sub>n</sub> with one to four heteroatoms selected independently from N, O and S;  $R-Y-C(O)-(alkyl)_n$  or  $R-C(O)-Y-(alkyl)_n$ , wherein each R independently is H, alkyl, alkenyl,  
 15 cycloalkyl, aryl or heterocyclyl as defined above, each of which is optionally substituted, Y is O or NH; each s and n is independently 0 or 1;

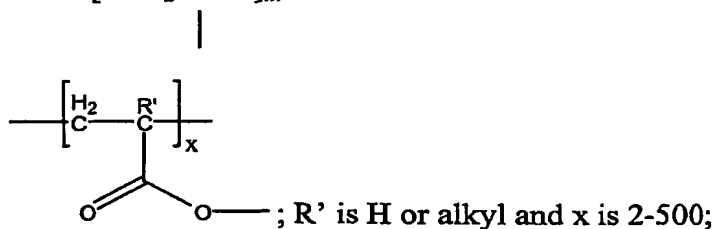
- or at one or both of the C-atom and  $Z_3$ , as given in the above formula (I),  $R_3$  and  $R_4$  form together with said C-atom or, respectively,  $Z_3$ , wherein they are attached to, an optionally substituted, saturated, partially saturated or aromatic, mono- or poly-  
 20 cyclic ring system of 5 to 20 carbon and, optionally, hetero ring atoms, whereby the optional hetero ring atoms are selected from N, O and/or S; and  $R_2$  is a monovalent radical as defined for  $R_3$  and  $R_4$  above, or forms a bond between the C-atom and  $Z_1$  or, respectively, between  $Z_3$  and  $Z_2$ , or forms a bond in the ring system formed by  $R_3$  and  $R_4$  between said C-atom or, respectively,  $Z_3$ , and a ring atom adjacent  
 25 thereto;

- or  $Z_3$  forms together with  $R_2$ , if present,  $R_3$  and  $R_4$ , which are attached thereto, a group  $-R'_5([Z_1-Z_2-R_6]_t Z_1-Z_2-R_5-H)_t$ , wherein each  $R'_5$  and  $R_5$  is independently optionally substituted alkyl, optionally substituted alkyl interrupted with one or more N, O and/or S, optionally substituted cycloalkyl, optionally substituted cycloalkylalkyl, optionally substituted cycloalkylcycloalkyl, optionally substituted aryl,  
 30 optionally substituted arylalkyl, optionally substituted arylalkylaryl, optionally substituted heterocyclyl, optionally substituted heterocyclylalkyl or optionally substituted heterocyclylalkylheterocyclyl, each  $R_6$  independently has a meaning as given for  $R'_5$  and  $R_5$  above,  $Z_1$  and  $Z_2$  are each independently as defined above, t is 1-3

and k is chosen so that the molecular weight of the resulting compound of formula (I) is within 200 to 10000 g/mol;

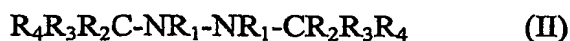
- 5 or  $Z_3$  together with  $R_2$ , if present,  $R_3$  and  $R_4$ , which are attached thereto, represent a linking group  $-R_8-$  to form  $R_2R_3R_4C-Z_1-Z_2-R_8-[U]_x$  which denotes a recurring structural unit of a polymer, wherein  $R_8$  is a linking bond or alkyl, cycloalkyl, heterocyclyl or aryl;

U is a  $[-CH_2-CR'-]_x$ , or



- 10 or the two  $R_3$ 's, as given in the above formula (I), form together with the  $-(R_2R_4)C-Z_1-Z_2-Z_3((R_2)_rR_4)-$  moiety an optionally substituted, saturated, partially saturated or aromatic, mono- or polycyclic ring system of 5 to 20 carbon and, optionally, further hetero ring atoms, whereby the further hetero ring atoms are selected from one or two of N, O and/or S; and wherein  $Z_1$  to  $Z_3$ , r and  $R_2$  to  $R_4$  are as defined above;
- 15 and the compound of formula (I') is selected from the compounds of formulae (II)-(IV):

a compound of formula (II)



- wherein the two  $R_1$ 's form together a bond, or each  $R_1$  independently is H or forms a bond together with  $R_2$  present at the adjacent C-atom as defined above;
- 20 a compound of formula (III)



wherein the two  $R_1$ 's form together a bond; or

a compound of formula (IV)

- 25  $R_4R_3R_2C-O-O-CR_2R_3R_4 \quad (IV)$

wherein in the above formulae (II)-(IV)  $R_1$  to  $R_4$  are defined as above;

as well as an oxide of N as  $Z_1$ - $Z_3$ , a salt, an ester or an amide thereof, or a mixture of two or more compounds of formula (I') as defined above; and

(c) optionally an effective amount of a further flame retardant other than the compound of formula (I'),

- 5 with the proviso that any optional further flame retardant is other than a halogenated flame retardant compound.

15. A composition of claim 14, wherein the compound of formula (I') is a compound of formula (I) or a compound of formula (IIb) or (IIc) as defined in any of claims 1-11.

- 10 16. A composition of claim 14 or 15, which comprises a synergistic mixture of the compound of formula of (I') and one or more further FR selected from a non-halogenated N-hydrocarbyloxy substituted (NOR) hindered amine flame retardant, aluminium compounds, such as aluminium trihydrate, boron compounds, magnesium hydroxide and/or intumescent systems, e.g. expandable graphite.

15

**(57) Abstract**

The present invention is directed a method of flame retarding a polymeric substrate using a specific group of azo and peroxide derivatives as flame retardants, to flame retardant compositions as well as to novel azo compounds usable as flame retarding compounds



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